When is Mineralization Really Template Directed?

Beamline: X22B

Technique: Grazing Incidence X-ray Diffraction from a Liquid Surface

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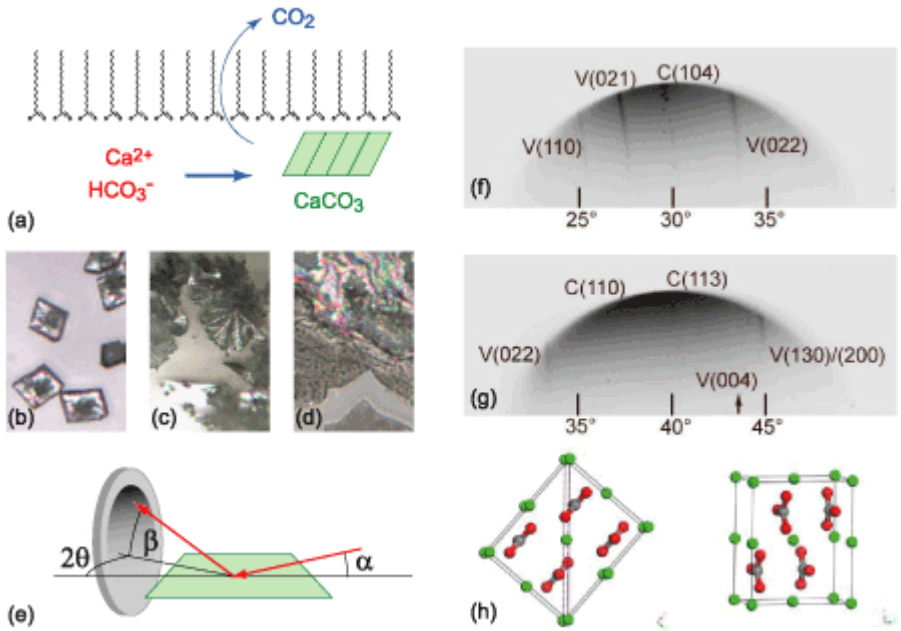
Motivation: In biological mineralization, proteins and other macromolecules direct the formation of non-equilibrium morphologies and polytypes. In the case of $CaCO_3$ minerals, studies have shown that organic templates such as fatty acid monolayers can selectively nucleate certain polytypes. Very influential reports from 1988 attributed this to stereochemical templating, although no direct structural evidence could be obtained at early growth times. Using in-situ grazing incidence diffraction, we re-investigated these mineral recipes and looked for evidence of stereochemical recognition between crystal and template.



$CaCO_3$ nucleation at monolayers (a) can produce calcite rhombs (b), vaterite florets (c), or an amorphous film (c), depending on kinetics. In-situ surface x-ray scattering (e) obtains diffraction patterns (f,g) showing that a range of vaterite orientations (h) are present at the monolayer.

Results: Diffraction patterns from the mineralizing surface exhibit powder arcs and show conclusively that the vaterite polytype is not oriented to the organic template. Instead we found, by varying the supersaturation in template-independent ways, that kinetic effects are sufficient to select between calcite and vaterite. One way by which kinetics may be modified is the surface charge of the monolayer, which attracts Ca^{2+} cations from solution. The ratio of Ca^{2+} to surfactant molecules at the surface is much lower than the 1:2 ratio implied by stereochemical binding models.